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(54) **Process for decreasing acidity of a crude oil**

(57) An acidic crude oil (more especially one containing naphthenic acids) and an effective amount of an aqueous base solution are combined at conditions of pH and temperature sufficient to form an unstable emulsion of the acidic crude oil in the aqueous base solution. The

emulsion is broken to form a phase containing crude oil having a decreased acidity and aqueous phase containing residual base and neutralized acids. When the acidic crude oil also contains calcium then decrease in calcium content can also be achieved.

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Description

The present invention relates to a process for decreasing the acidity of a crude oil.

Whole crudes and crude fractions with high petroleum acid content such as those containing naphthenic acids are corrosive to the equipment used to extract, transport and process the crude.

Efforts to minimize naphthenic acid corrosion have included a number of approaches. U.S. Patent 5,182,013 refers to such recognized approaches as blending of higher naphthenic acid content oil with low naphthenic acid content oil. Additionally, a variety of attempts have been made to address the problem by using corrosion inhibitors for the metal surfaces of equipment exposed to the acids, or by neutralizing and removing the acids from the oil. For example, Kalichevsky and Kobe in *Petroleum Refining with Chemicals* (1956), Chapter 4, disclose various alkali treatments of crudes and crude fractions. U.S. Patent 4,199,440 which teaches the use of difficult-to-break caustic-in-oil emulsions discloses treatment of a liquid hydrocarbon with a dilute aqueous alkaline solution, specifically dilute aqueous NaOH or KOH. U.S. Patent 4,300,995 discloses the treatment of carbonous material particularly coal and its products, heavy oils, vacuum gas oil, petroleum resids having acidic functionalities with a dilute quaternary base such as tetramethylammonium hydroxide in a liquid (alcohol or water). IR data of the untreated crude show a peak at 3300-3600 cm^{-1} corresponding to a phenolic hydroxide (Example 6). The C^{13} NMR spectrum of O-methylated crude shows a signal at 55 ppm corresponding to a methyl phenoxide (Examples 3 and 4). This patent was aimed at improving yields and physical characteristics of the products and did not address the question of acidity reduction. Kalichevsky and Kobe as well as U.S. Patent 4,199,440 note, however, that a problem arises because certain aqueous base solutions form stable caustic-in-oil emulsions, necessitating use of only dilute aqueous base solutions.

While these processes have achieved varying degrees of success there is a continuing need to develop more efficient methods for treating acidic crudes.

SUMMARY OF THE INVENTION

A process for decreasing the acidity of an acidic crude oil comprising: contacting an acidic crude oil with an effective amount of an aqueous base solution at conditions of pH and temperature sufficient to form an unstable emulsion of the acidic crude oil in the aqueous base and breaking the emulsion to form a phase containing treated crude oil having a decreased acidity and aqueous phase containing residual base and neutralized acids.

The present invention may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not dis-

closed.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 describes the unstable oil in water emulsion treatment of the present invention as a standalone process.

Figure 2 describes the unstable oil in water emulsion treatment for removal of naphthenic acid from a crude oil at the well head integrated with a representative currently available process.

DETAILED DESCRIPTION OF THE INVENTION

Some crude oils contain organic acids that contribute to corrosion or fouling of refinery equipment and that are difficult to separate from the processed oil. The organic acids generally fall within the category of naphthenic and other organic acids. Naphthenic acid is a generic term used to identify a mixture of organic acids present in petroleum stocks. Naphthenic acids may be present either alone or in combination with other organic acids, such as phenols. Naphthenic acids alone or in combination with other organic acids can cause corrosion at temperatures ranging from about 65°C (150°F) to 420°C (790°F).

The crudes that may be used are any naphthenic acid-containing whole crude oils that are liquid or liquefiable at the temperatures at which the present invention is carried out. As used herein the term whole crudes means unrefined, non-distilled crudes. The acidic crudes are preferably whole crudes. However, acidic fractions of whole crudes such as vacuum gas oil also may be treated. An additional benefit of the treatment process is the absence or substantial absence of stable emulsion formation. Stable emulsion formation is undesirable and a particular problem that is encountered during treatment of acidic crudes with aqueous bases. The formation of a stable crude oil-aqueous emulsion tends to interfere with the efficient separation of the crude oil and aqueous phases and thus with recovery of the treated crude oil. Thus, in addition to their corrosivity such acids must be removed from the crude oil due to their tendency to encourage stable emulsion formation during processing, especially desalting processes.

Unexpectedly, and contrary to prior art teachings, Applicants have discovered that acidic crudes, e.g., those containing naphthenic acids, may be treated by mixing the crude with an effective amount of an aqueous base at conditions of pH and temperature sufficient to form an unstable emulsion of the crude oil in the aqueous base ("oil-in-aqueous base") and coalescing (destabilizing) the emulsion to produce a first phase containing a treated or final crude oil having a reduced or essential absence of acidity and a second phase containing at least the remaining unreacted aqueous base. Neutralized acids, such as the corresponding naphthenate are present in the second phase or at the interface between

the first and second phases. When the starting acidic crude is a calcium-containing crude, the process produces a treated crude having a decreased acidity and calcium content. Typically, the calcium is present as an insoluble, calcium-containing phase that is disposed between the first and second phases when the emulsion is broken. Optionally, the aqueous phase containing excess base may be recovered and reused in either a batch or continuous process to contact additional untreated crude, typically until the pH of the recovered aqueous phase reaches a pH of 8.0. Thus, desirably the aqueous phase is not completely neutralized and excess base is present in the recovered aqueous base.

The aqueous base is suitably an aqueous Group IA or IIA hydroxide, preferably NaOH or KOH solution, more preferably NaOH, having a pH of at least 8, preferably 8 to 12.

An unstable emulsion is formed by adding the acidic crude oil with only mild agitation to the aqueous base in a sufficient ratio to produce a dispersion of oil in a continuous aqueous base phase. The crude oil should be added to the aqueous base rather than the aqueous base being added to the crude oil, in order to minimize formation of a stable aqueous base-in-oil emulsion. A ratio of 1:3 to 1:15, preferably 1:3 to 1:4 of oil to aqueous base is used based on the weight of oil and water. A stable emulsion will form if the ratio of oil to aqueous base is 1:1 or less. The weight percent of base in water ranges from 0.5 to 3.0%. Droplet size of from 10-50 microns preferably 20-50 microns is typically needed. Contacting of the crude oil and aqueous phase should be carried out for a period of time sufficient to disperse the oil in the aqueous phase preferably to cause at least 50% by weight, more preferably at least 80%, most preferably 90% of the oil in the aqueous phase.

Contacting is carried out until the pH of the basic aqueous phase decreases to about 8. Until such time the aqueous phase may be recycled for use to treat additional starting acidic crude oil.

The contacting of the crude oil and aqueous base solution to form the unstable emulsion is carried out at temperature typically from about 10°C to 40°C. At temperatures of greater than 40°C the probability of forming a stable emulsion increases.

Contacting times depend on the nature of the crude to be treated, its acid content, and the amount and type of aqueous base added, but typically may be carried out for from about 2 minutes to about 2 hours. Similarly, time needed to coalesce or destabilize the emulsion will vary but typically 1-2 minutes is a minimum. Oil type, particle size and distribution of oil droplets affects coalescence/destabilization rates. Gravity or an electrostatic field may be applied to facilitate demulsification. Destabilizing or demulsifying additives or agents are not required, but may be used to enhance the rate of emulsion breaking.

Additionally, there may be added to the basic aqueous phase prior to contacting with the starting acidic

crude oil a sufficient amount of non-ionic surfactant, preferably of a straight chain ethoxylated alcohol having a chain length of from 12 to 18 carbon atoms and from 10 to 50 ethoxy groups typically in an amount of less than 0.001 wt% based on weight of crude oil to enhance formation of the unstable emulsion.

The emulsion may be broken by any suitable method, preferably by gravity coalescence to generate a treated crude having a reduced acidity and an aqueous phase containing naphenate salts.

The bases and surfactants suitable for use in the process may be purchased commercially or synthesized using known procedures.

The concentration of acid in the crude oil is typically expressed as an acid neutralization number or acid number, which is the number of milligrams of KOH required to neutralize the acidity of one gram of oil. It may be determined according to ASTM D-664. Any acidic crude may be treated according to the present invention, for example, crudes having an acid neutralization number of from 0.5 to 10 mg KOH/g acid. Typically, the decrease in acid content may be determined by a decrease in the neutralization number or in the intensity of the carboxyl band in the infrared spectrum at about 1708 cm⁻¹. Whole crude oils with acid numbers of about 1.0 and lower are considered to be of moderate to low corrosivity. Crudes with acid numbers greater than 1.5 are considered corrosive. Acidic crudes having free carboxyl groups may be effectively treated using the process of the present invention.

Whole crude oils are very complex mixtures containing a wide range of contaminants and in which a large number of competing reactions may occur. Unexpectedly, in the current process not only is the acidity of the crude reduced but a reduction in calcium content is also effected.

The process of the present invention has utility in processes in which inhibiting or controlling liquid phase corrosion, e.g., of metal surfaces, is desired. More generally, the present invention may be used in applications in which a reduction in the acidity of an acidic whole crude would be beneficial.

By way of example the process is especially beneficial for treatment to decrease acidity and calcium content of acidic crude oils at the wellhead. Such crudes typically contain impurities such as naturally occurring or coproduced water and gases. In Figure 1 a full well stream containing whole acidic crude oil, water and gases is passed via line 1 to a separator 3, and separated into a gas stream, which is removed via line 2, a water stream containing trace amounts of oil which is removed via line 4 and combined with base, typically aqueous, from line 6 prior to entering contactor 7, and an oil stream containing trace amounts of water which is passed via line 5 to contactor 7. The upper water and base stream from line 4 and 6 and lower oil stream from line 5 are contacted in contactor 7 to form an unstable oil in aqueous base emulsion. Treated oil containing re-

residual water is drawn off overhead from contactor 7 via line 5a and passed to separator 8 to separate the treated oil from residual aqueous base. The lower phase of aqueous base containing residual treated oil is drawn off below via line 4a and passed to separator 9 from which aqueous base is recovered and passed out via line 10 and may be recycled to line 6 or disposed of, and residual treated oil is passed via line 9a to stabilizer tower 12. From separator 8 treated oil is removed via line 8b to stabilizer tower 12 while aqueous base is removed via line 8a to separator 9. From stabilizer tower 12 gases and volatiles are removed through line 13 and treated oil via line 11.

In Figure 2 the process is shown integrated into a currently available process, thus 3, 8, 9 and 12 and the lines connecting them represent a process that exists typically at the wellhead for the separation of the full well stream line 1 into gas stream via line 2, treated oil stream via line 11, and aqueous base line 10. The streams leaving the separator 3 are gas via line 2, water containing traces of oil via line 4, and oil stream containing traces of water via line 5. The water containing trace amounts of oil passes via line 4 to a separator 9 which removes trace oil. The water is then injected into the well. The oil stream 5 passes to a separator 8 which removes traces of water. Finally the oil is passed via line 8b to a stabilizer tower 12 where residual gas and volatiles are removed overhead via line 13 and treated oil via line 11. The new contactor is represented by the block 7 and the lines connecting it to a typical current process. The feeds to contactor 7 are water via line 4 and the oil via line 5. Prior to entering contactor 7, base added via line 6 to the water line 4 as described with respect to Figure 1 above. In contactor 7, the aqueous base from lines 4 and 6 and oil from line 5 are mixed so as to form the unstable oil-in-caustic emulsion as described with respect to Figure 1, and after a sufficient mixing time, the phases are allowed to separate. The separated aqueous base-containing residual oil phase is passed via line 4a to separator 9, and the separated oil phase to separator 8. Valves V1 and V2 are provided to allow operation of the crude oil treatment process either in whole or in part with, or without the portions of the process associated with forming the unstable emulsion and separating the resulting products (contactor 7 and lines connected thereto) described in Figure 1. The reference numerals in Figure 2 correspond to the same numerals in Figure 1.

The present invention may be demonstrated with reference to the following non-limiting examples.

Example 1

25g of Bolobo 2/4 (Chad crude oil) was added to 80 ml of 1.5 wt% NaOH solution in a separatory funnel. The oil/water mixture was shaken gently on a wrist shaker for 20 minutes. It was determined by droplet size measurements using a Coulter Multisizer 11 instrument that

greater than 90% of the crude oil was dispersed as an oil-in-water emulsion. After contacting for 20 minutes, the shaker was stopped and the emulsion allowed to stand. In 10 minutes the emulsion destabilized and a yellowish lower aqueous phase separated out. The aqueous phase pH of 8.0 and the treated oil were separated. The aqueous phase was reused by repeating the above experiment (Example 2) with addition of a fresh batch of 20g of Bolobo 2/4 crude. Two treated crude oil samples were generated from the experiment:

Sample #1 in which the acidic crude was treated with fresh aqueous NaOH.

Sample #2 in which a second batch of acidic crude was treated with reused aqueous phase.

Both treated crude samples were centrifuged to remove traces of aqueous phase and then analyzed by the ASTM D-664 method. A 100% neutralization of the acid was observed. The corresponding aqueous phases from Samples #1 and #2 were neutralized with concentrated HCl to pH = 3 and the petroleum acids were precipitated. The precipitated acids were extracted with methylene chloride and analyzed by infrared spectroscopy. A characteristic IR absorption at 1703 cm^{-1} was observed confirming the extraction of naphthenic acid into the aqueous phase.

Example 2

The procedure of Example 1 was repeated using ammonium hydroxide instead of sodium hydroxide. No reduction in acidity or extraction of acid into the aqueous phase was observed.

Example 3

The procedure of Example 1 was repeated using tetrabutyl ammonium hydroxide instead of sodium hydroxide. A stable unbreakable emulsion resulted. The treated crude could not be separated from the aqueous phase.

Example 4

A Chad crude (Kome 6/1) that was high in calcium (916 ppm) and in acidity was subjected to the procedure of Example 1. In addition to reduction in acidity, the calcium in the treated crude was reduced from 800 ppm to 32 ppm (96% reduction in calcium). A calcium-containing layer formed between the treated crude and aqueous phase when the unstable emulsion broke.

Claims

1. A process for decreasing the acidity of an acidic crude oil, comprising:
 - (a) forming an unstable emulsion of the acidic

crude oil in an aqueous base solution:

(b) breaking the unstable emulsion to produce a first phase containing treated crude oil having a decreased acidity and a second aqueous phase containing residual base and neutralized acids.

2. The process of claim 1, wherein the acidic crude oil is a calcium-containing acidic crude oil. 10
3. The process of claim 2, wherein the breaking of the emulsion produces a third phase, disposed between and separable from the first and second phases, containing calcium compounds. 15
4. The process of claim 2 or claim 3, for decreasing the acidity and calcium content of a calcium-containing acidic crude oil, comprising: 20
 - (a) separating the crude oil into a first stream containing primarily water and trace amounts of the crude oil and a second stream containing primarily crude oil and trace amounts of water; 25
 - (b) combining the first stream with aqueous base; 30
 - (c) countercurrently contacting the first and second stream to produce an unstable oil in aqueous base emulsion; 35
 - (d) recovering a lower phase containing primarily aqueous base and residual treated oil and an upper phase containing primarily treated oil and residual aqueous base; 40
 - (e) separating the upper phase from step (d) into a treated oil stream containing residual water and an aqueous base stream containing residual treated oil; 45
 - (f) passing the lower phase of step (d) and the aqueous base stream of step (e) to a separator to recover an aqueous base stream and treated oil stream; 50
 - (g) passing the treated oil stream from step (e) and the treated oil stream from step (f) to a stabilizer tower; 55
 - (h) degassing and recovering the treated oil stream.
5. The process of any preceding claim, wherein the acidic crude oil in the aqueous emulsion has a drop-let size of 10 to 50 microns.

6. The process of any preceding claim, wherein the acidic crude oil contains naphthenic acids.
7. The process of any preceding claim, wherein the base is present in an amount of from about 0.5 to 3 wt% in the aqueous base solution.
8. The process of any preceding claim, 1 wherein a weight ratio of acidic crude oil to aqueous base solution of 1:3 to 1:15 is employed in producing the unstable emulsion.
9. The process of any preceding claim, wherein the base is selected from Group IA and IIA hydroxides, preferably NaOH or KOH.
10. The process of any preceding claim, wherein the aqueous base solution further contains a non-ionic ethoxylated alcohol surfactant having from 10 to 50 ethoxy groups and a chain length of 12 to 18 carbon atoms.

FIGURE 1

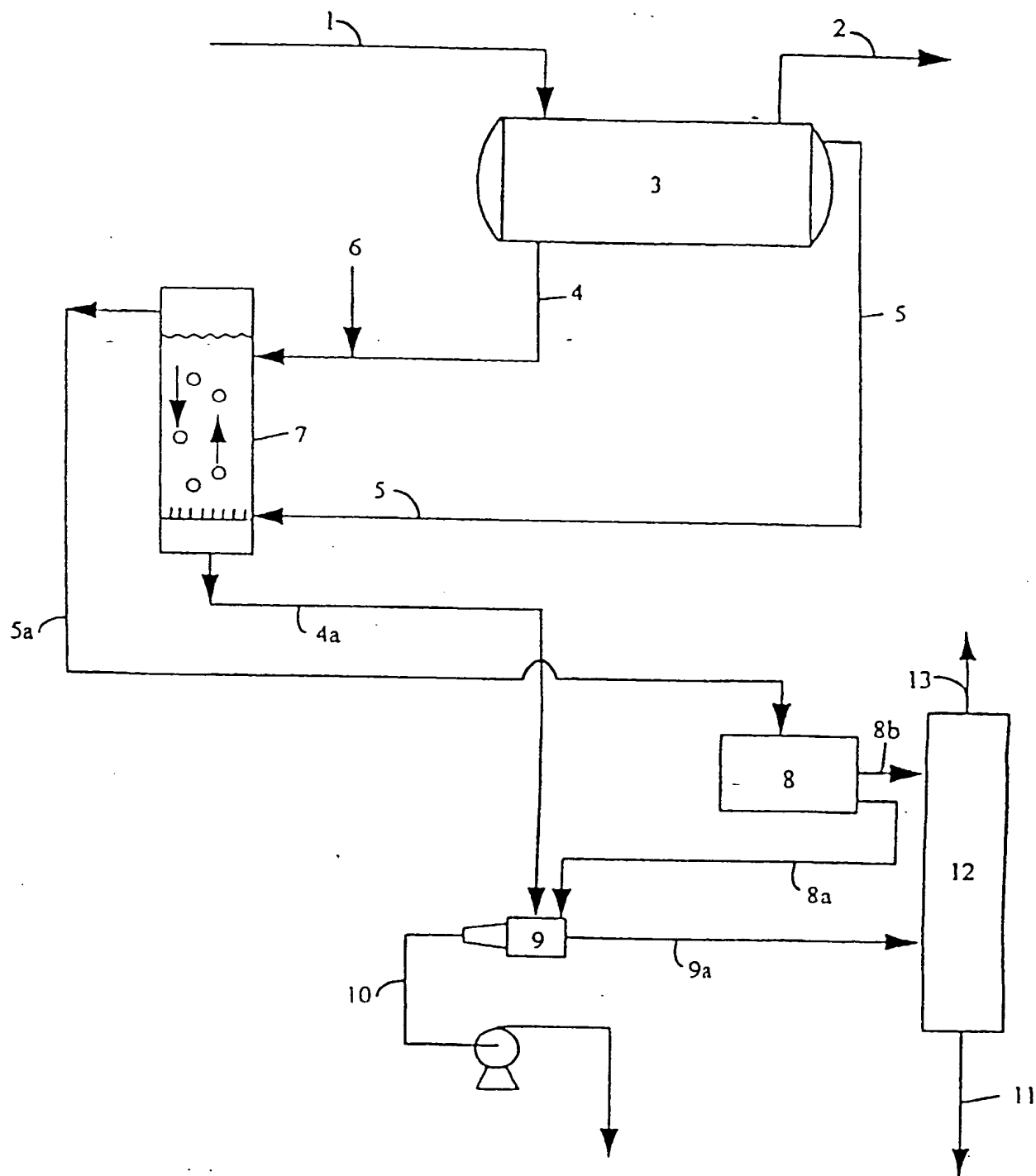
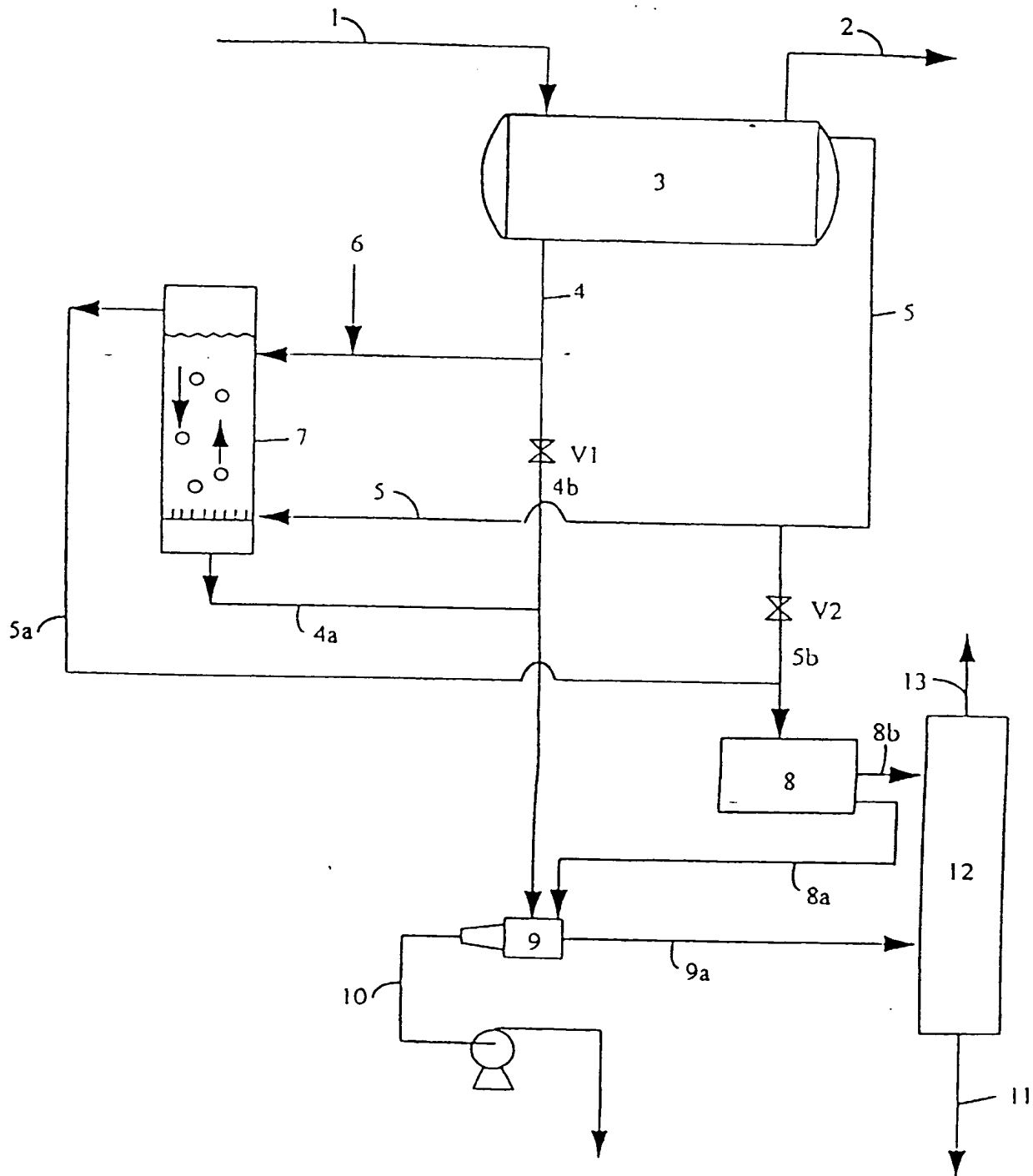


FIGURE 2



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Place of search THE HAGUE		Date of completion of the search 16 December 1998	Examiner Zuurdeeg, B
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